CHEMISTRY AND TECHNOLOGY OF ORGANIC SUBSTANCES, MATERIALS AND GOODS

УДК 667.633.2

M. V. Zhuravleva, PhD student (BSTU);
N. P. Ivanova, PhD (Chemistry), assistant professor (BSTU);
T. A. Zharskaya, PhD (Engineering), assistant professor (BSTU);
E. T. Krut'ko, D.Sc. (Engineering), professor (BSTU)

MODIFICATION OF EPOXY RESIN BY OLIGOMALEIMIDOHYDROXYPHENYLENE

The article is devoted to development and research of new film materials on the basis of epoxy pitches with the improved properties. The assessment of protective properties is defined by electrochemical methods of research, and also with physic-mechanical that gives the most complete idea of the corrosion processes proceeding under a paint and varnish film. Data of researches allowed to correct covering structure for separate scopes for the purpose of achievement of high extent of protection of metal surfaces.

Introduction. Currently, application of paint coatings is one of the most common and reliable methods of protecting metal surfaces from corrosion.

Paint coatings are cheaper compared with other types of protective coatings, can be easily repaired if damaged during use, and are diverse in appearance and color.

Paint coatings (PC) are particularly effective as the outer layer in the combined coatings, they are applicable for protection of any structures, regardless of the size and material of the substrate. Normally, the PCs are multilayered, it reduces the porosity of the coating and the propensity to filiform corrosion.

The advantages of paint coatings over other types of coatings are convenience and ease of application, low cost, and the ability to restore the coating with the desired properties and color.

The proportion of coating compositions based on condensation film-formers (epoxy, carbamide-melamine-formaldehyde, alkyd, etc.) is steadily increasing. This ensured the creation of materials with high chemical resistance towards aggressive media and set the task of making an objective assessment of the resulting protective systems durability.

It is known that under operating conditions it takes years to test the protective properties of coatings, which satisfies neither the developers nor the producers who need continuous testing. Accelerated tests provide information on the stability of the coating under its forced crush conditions simulating natural mechanism of aging in a short time test. Electrochemical methods are used for such accelerated test methods.

Protective properties of paint coatings are determined by the amount of physical and chemical properties which can be reduced to four characteristics [1]:

1) The electrochemical and insulation properties of coatings;

2) The ability of the films to slow diffusion and corrosion reactants transfer to the metal surface;

3) The ability of coatings to passivate or protect metal electrochemically;

4) The adhesion and the mechanical properties of coatings.

Main part. The aim of this work was the development and research of new film materials based on epoxy diane resins with improved protective properties.

The object of research is an industrially produced E-41 epoxy resin in a solution (E-41r) (TU 6-10-607-78). The resin is a solution of E-41 resin with a mass fraction (66 ± 2)% in a mixture of xylene (GOST 9410-78 GOST 9949-76) and acetone (GOST 2768-84) in the ratio 4 : 3 by weight. A solution of E-41 resin in a mixture of xylene and acetone (Resin E-41r) is used for the manufacture of coating compositions for various purposes. E-41 r resin refers to medium molecular weight (mol. weight 900-2000) epoxy diane resins. Its density is 1.03-1.06 g/cm^3. The product of copolycondensation of low molecular weight epoxy resin E-40 with diphenylol propane is represented by the formula shown in Fig. 1.

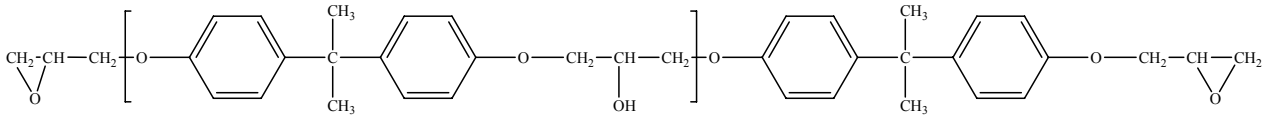

Fig. 1. Chemical structure of an epoxy-diane oligomer

Physico-chemical characteristics of E-41 r resin are shown in Table 1. The film-forming compositions were prepared by introducing a 10% modifier solution in dimethyl formamide into E-41 r in the concentration range of 0.5-5.0 wt.%, followed by stirring until a homogeneous mass. E-45 (TU 6-10-1429-79 with alternations № 2) hardener which is a low molecular weighed polyamide resin solution in xylene was used in an amount of 14% by dry weight of a resin residue. Films from the above mentioned solutions were poured on various substrates (glass and carbon steel). Hardening of modified epokxydiane compositions was performed at 110°C for 140 min.

Adhesion strength of the formed coatings was determined by the standard technique in accordance with ISO 2409 and GOST 15140-78 using the cross-hatch test with a back impact. The essence of the method is to cross cut the finished coating using "Adgozometer PH" device as well as to assess visually the state of the coating following the impact exerted by "Udar-Tester" device on the reverse side of the plate in the place of cuts.

The state of coatings was compared to the standard classification, the adhesion strength being measured in points. Impact strength of coating samples was evaluated using the "Udar-Tester" device in accordance with ISO 6272 and GOST 4765-73. The technique for determining an impact strength of films (measured in centimeters) is based on the instantaneous deformation of the painted metal plate in the course of the free fall of a load on the specimen. This technique is implemented using the device "Udar-Tester" which is intended to control the toughness of polymer, powder and paint coatings.

The hardness of paint coatings was determined on the pendulum tester (ISO 1522). The essence of the technique is to determine the decay time (number of oscillations) of the pendulum on its contact with the paint coating. Hardness is determined by the ratio of the number of oscillations of the coated sample to the number of oscillations of the sample without coating.

To assess the protective properties and select the modifier concentration in the polymer coating it is necessary to study the time dependence of the stationary potential of a carbon steel-coating system and to remove polarization curves.

Potential measurement of the metal-coating system in a 3% NaCl solution was carried out in a silver-chloride reference electrode scale at 20°C for 24 hours, then the potential values were recounted into a standard hydrogen electrode scale.

Reading off the anodic polarization curves in 3% NaCl was carried out using a potentiostat PI-50-1 and a driving voltage programmer PR-8. Tests were performed in a three electrode electrochemical cell (Fig. 2).

The value of the equilibrium potential was being determined for 5 min. following the immersion of the sample into the solution. Measurements were carried out in a potentiostatic mode at a step change potential in 20 mV, the time current method at each potential being 1 min. The test objects were 0.8 rs carbon steel plates (thickness 0.8-1.0 mm, size 15×70 mm) with an epoxy polymer coating on both sides.

To enhance the protective capacity of a coating a modifier has been introduced, the concentration being 0.5–3.0%.

The preparation of the substrate surface was performed mechanically (grinding) and chemically (degreasing). The edges of the test samples were protected by the material under study.

Table 1

Physical and chemical parameters of E-41 resin

Parameter name	Highest quality standard category
Resin solution appearance	Homogeneous transparent liquid.
Film appearance	Pure pouring on the glass. Insignificant pimple is allowed
Iodimetric scale colour, mg I_2/100 cm^3, not darker	30
B3-246 (B3-4) funnel viscosity with a 4 mm jet size at (20,0±0,5) ºC, c	80-130
Non-volatile mass content , %	66±2
Epoxy groups mass content on a dry resin basis , %	6.8-8.3
Chlorine ion mass content (on a dry resin basis), %, not more	0.0045
Saponifiable chlorine mass content (on a dry resin basis), %, not more	0.25

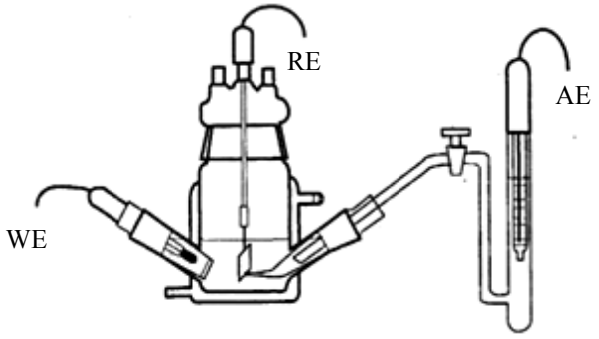

Fig. 2. Electrochemical cell CGE-2:
WE – w ork electrode (carbon steel 08 rs with polymer coating); AE – auxiliary electrode (platinum);
RE – reference electrode (silver-chloride electrode)

Coating compositions were applied manually in one layer (brush painting), the coating thickness being 20-25μm. Drying was performed at 120°C for 140 min. Before electrochemical research samples were degreased with acetone and dried in air.

Oligomaleimidohydroxyphenylene (OMIHPH) solution in dimethylformamide (DMF) was used as an epoxy resin modifier.

OMIHPH synthesis is performed in a three-step process. Primarily oligoaminohydroxyphenylene is synthesized from n-aminophenol in the presence of catalytic amounts of n-toluene sulphonic acid (n-TSA).

P-aminophenol and 7 wt % n-TSA were charged into a flask equipped with a stirrer, a thermometer, and a reflux condenser. The reaction is conducted in the melt at 250°C for 6 hours in a nitrogen medium (Fig. 3).

The product is isolated from the reaction mixture by DMF extraction followed by re-precipitation into diethyl ether, whereupon for the final removal of an unreacted monomer it is washed with 10% aqueous ammonia solution and distilled water. Washed oligomer is dried to a fixed mass in a vacuum drying furnace at 60°C. The resulting compound is a powdered black product. The yield is 70–80%.

Thereupon oligoaminohydroxyphenylene reacts with maleic anhydride to form oligoamide acid, which is further subjected to dehydrocyclization in an imidized mixture (Fig. 4).

The research results of the operating characteristics of compositions are shown in Table 2.

P-aminophenol and 7 wt % n-TSA were charged into a flask equipped with a stirrer, a thermometer, and a reflux condenser. The reaction is conducted in the melt at 250°C for 6 hours in a nitrogen medium (Fig. 3).

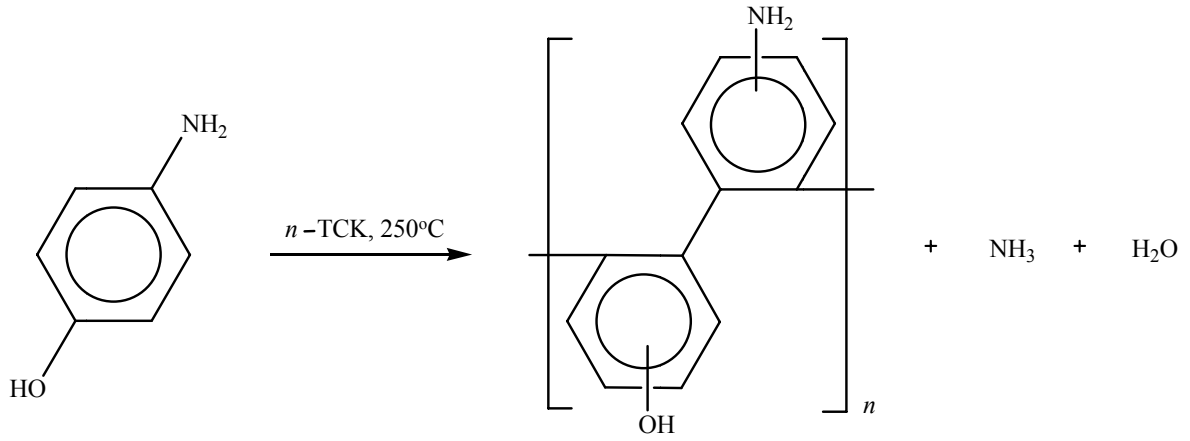

Fig. 3. Synthesis scheme of oligoamidohydroxyphenylene

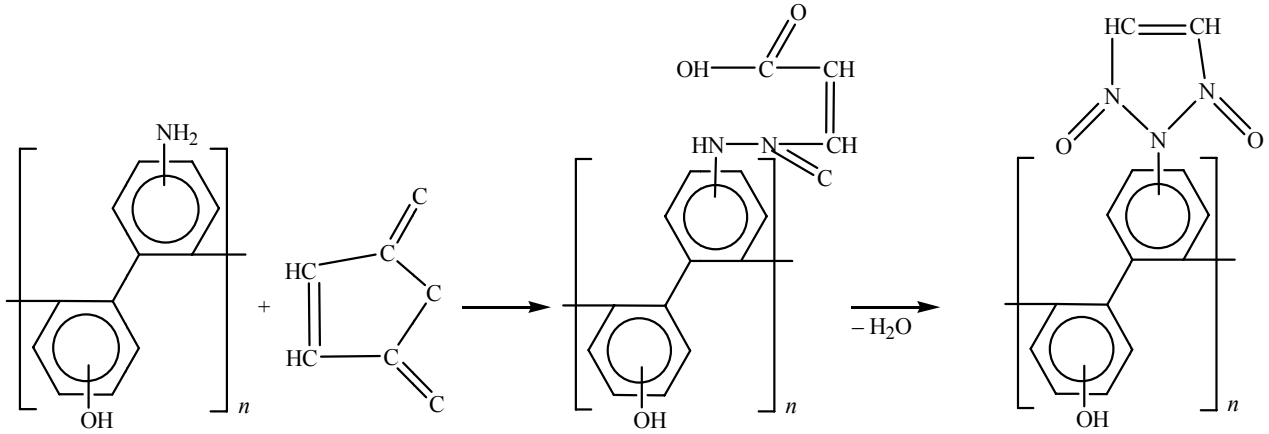

Fig. 4. Synthesis scheme of oligoaminohydroxyphenylene

Table 2

Adhesion and strength properties of epoxydiane coatings on steel substrates (heatup 110°C, 140 min)

OMIHPH content, %	Hardness, r. u.	Adhesion to steel, grade	Impact strength, cm
0.0	0.66	1	2.5
0.5	0.79	1	16.5
1.0	0.82	0	19.0
2.0	0.85	0	20.0
3.0	0.84	0	18.0
4.0	0.82	1	13.0
5.0	0.77	2	9.0

The product is isolated from the reaction mixture by DMF extraction followed by reprecipitation into diethyl ether, whereupon for the final removal of an unreacted monomer it is washed with 10% aqueous ammonia solution and distilled water. Washed oligomer is dried to a fixed mass in a vacuum drying furnace at 60°C. The resulting compound is a powdered black product. The yield is 70-80%.

Thereupon oligoaminohydroxyphenylene reacts with maleic anhydride to form oligoamide acid, which is further subjected to dehydrocyclization in an imidized mixture (Fig. 4).

The research results of the operating characteristics of compositions are shown in Table 2.

As seen from Table 2, in the presence of modifiers (1.0–3.0%) and curing temperature (100°C) the produced modified compositions are characterized by enhanced coating hardness, impact strength and adhesion. Further increase of the modifier content in the polymer composition results in the degradation of the mechanical properties of the protective coating. Protective and mechanical properties of coatings are interconnected and mutually affect one another. Deterioration of such film properties as a diffusion barrier will immediately lead to a decrease in adhesion due to the development of the corrosion process under the film. Therefore, the adhesion itself, no matter how good it may be, cannot provide a long-term protection of the metal from corrosion. Similarly, long-term coating protection with high diffusion limitations, but with weak adhesion can't be provided either [2]. Stationary potential dependencies of the system 'metal- coating' within 24 h are shown in Fig. 5.

Shift value of the stationary potentials of corrosion systems 'substrate-coating' to the electronegative side may be due to the anodic reaction of metal ionization [1].

For samples with epoxy polymer coating the stationary potential value becomes more electropositive compared to carbon steel.

Research data of the anodic behavior of steel with the test polymer lacquer coating in a 3% NaCl solution are shown in Fig. 6.

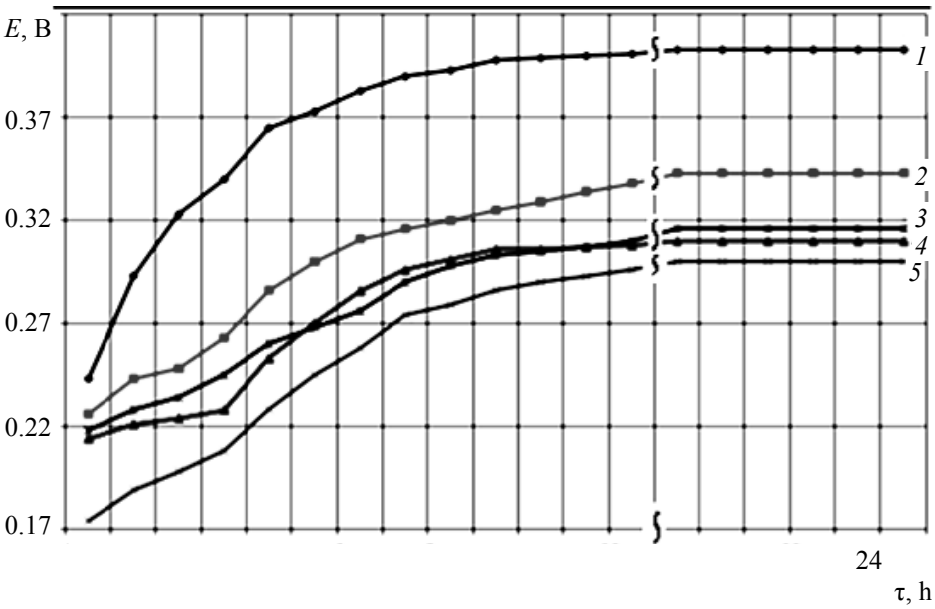

Fig. 5. Stationary potential dependencies of the 'substrate-coating' system in 3% NaCl: *1* – steel; *2* – PC; *3* – PC + 0.5% modifier; *4* – PC + 1% modifier; *5* – PC + 3% modifier

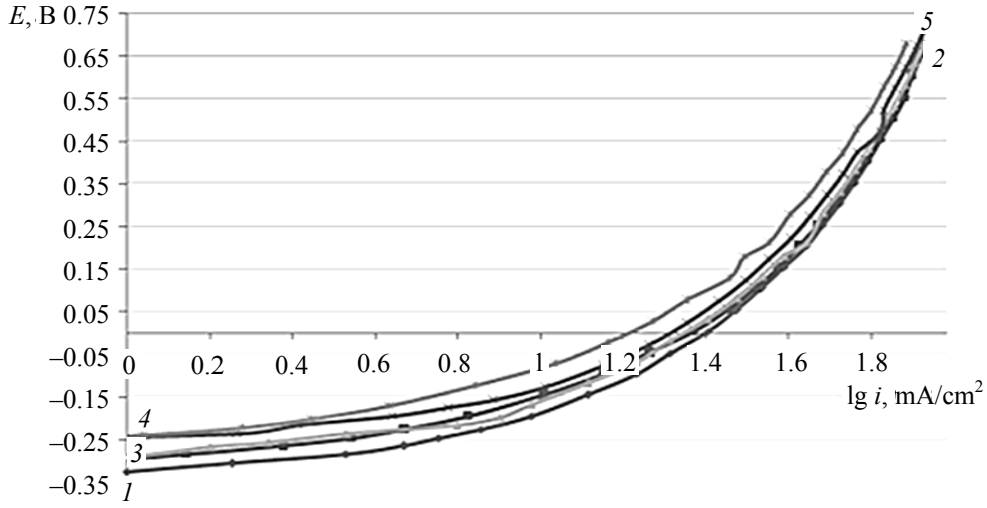

Fig. 6. Potentiostatic polarization curves in semilog coordinates:
1 – steel; *2* – PC; *3* – PC + 0.5% modifier; *4* – PC + 1% modifier; *5* – PC + 3% modifier

Tafel slopes b of all anodic curves are practically the same in the potential range 0.25-0.35 V (Table 3).

It is assumed that iron surface having been covered with polymer coating, the mechanism of its active dissolving doesn't change. Dissolution is in the pores of the coating, and the inhibiting effect is due to a decrease of the effective surface of the dissolving metal.

Extrapolation of the linear sections of the polarization curves (Fig. 7) up to the measured stationary potential value E_{24} makes it possible to determine the corrosion rate.

Table 3 shows the dissolution rates of uncoated and lacquered iron as well as those of the iron with and without the modifier applied.

Based on the data obtained, we can conclude that polymer coatings inhibit iron corrosion. Carbon steel 08 rs in 3% NaCl corrodes with a velocity 0.804 mA/cm^2. Application of the epoxy polymer coating with a 3% modifier reduces the corrosion rate as much as 7.3 times. Thus, the introduction of a modifier into a polymer coating can improve the corrosion resistance of a system. I this case the corrosion current density decreases (Fig. 8), and the polarization curves are shifted to lower currents (Fig. 6).

Table 3

Iron corrosion rates in 3% NaCl

Test sample	E, V	lg *i*, mA/cm^2	*i*, mA/cm^2	*b*, V
Carbon steel 08 rs	–0.402	–0.095	0.804	–0.21
Carbon steel 08 rs – PC	–0.325	–0.200	0.631	–0.12
Carbon steel 08 rs – PC + 0.5% modifier	–0.311	–0.210	0.617	–0.11
Carbon steel 08 rs – PC + 1.0% modifier	–0.305	–0.290	0.510	–0.10
Carbon steel 08 rs – PC + 3.0% modifier	–0.316	–0.945	0.110	–0.08

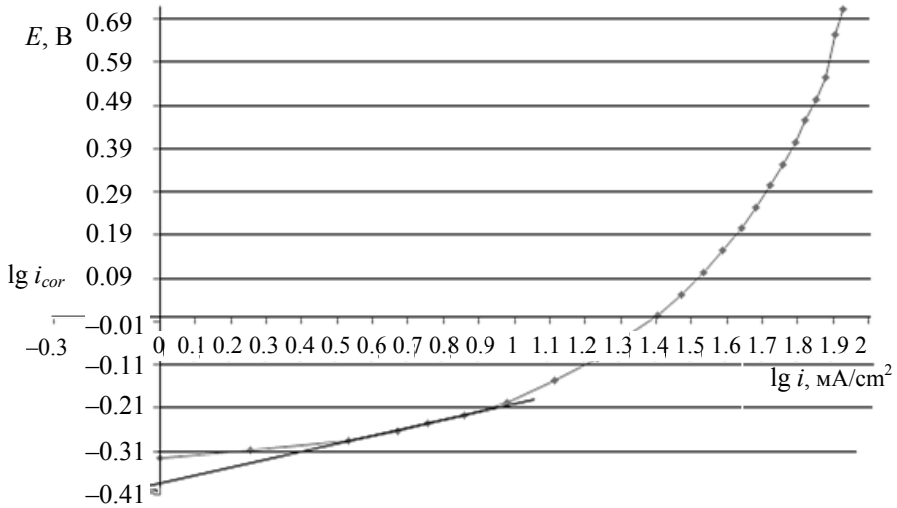

Fig. 7. Anodic polarization curve. Sample without coating E24 = 0.402 V; *i* = 0.804 mA/cm^2

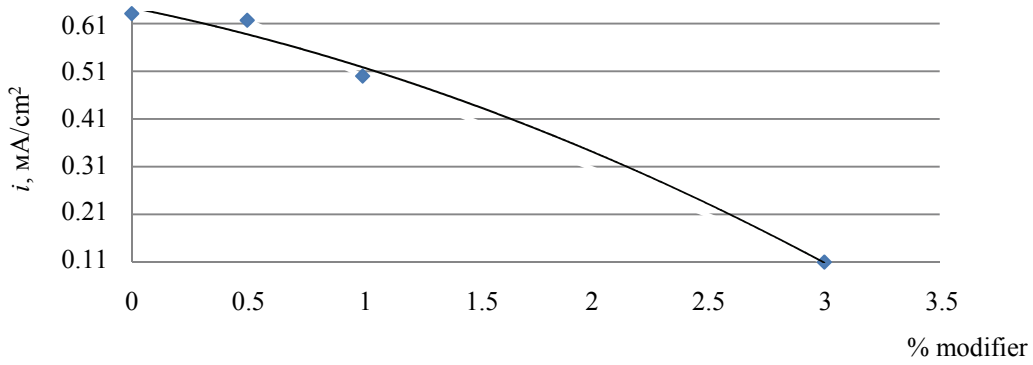

Fig. 8. Corrosion current dependence on the percentage of a coated modifier

In terms of the obtained data we can conclude that polymer paint coatings on the basis of oligohydroxymaleimidophenylene modified epoxy resins, inhibit carbon steel corrosion in a much greater degree than do unmodified epoxy coatings.

Conclusion. Experimental studies have shown that the additional evaluation of the protective properties of coatings by electrochemical methods in conjunction with conventional methods of research (inherent for coating industry) provides better understanding of the corrosion processes which proceed beneath the coating surface. These methods allow us to estimate their effect on the concentrations of the modifier (0.5–5.0%). These studies allowed to improve the coating composition for specific applications in order to achieve a high degree of protection of metal surfaces.

Modification of epoxy oligomers by oligomaleimidohydroxyphenylene is one of the ways to change the properties of the coatings obtained. These modifications are due to the introduction of various polyfunctional fragments capable of reacting with active epoxy oligomer groups at different stages of the process of a protective layer formation.

OMIHPH modifier introduction in the polymer coating can improve the system corrosion resistance approximately 7 times as much, in this case current density of iron corrosion reduces in the range of 0.80-0.11 mA / cm2, and the polarization curves are shifted to lower currents.

References

1. Розенфельд И. Л., Рубинштейн Ф. И. Антикоррозионные грунтовки и ингибированные лакокрасочные покрытия. М.: Химия, 1980. 200 с.

2. Розенфельд И. Л. Ингибиторы коррозии. М.: Химия, 1977. 352 с.

Received 11.02.2014